SYNOPSIS FOR REGISTRATION FOR DOCTOR OF PHILOSOPHY DEGREE IN CHEMISTRY

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Title of Thesis : **Spectrophotometric Studies of Some Metal Ions, Drugs and Pesticides Using Organic Reagents in Industrial effluents.**

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1. TITLE OF THE THESIS

SPECTROPHOTOMETRIC STUDIES OF SOME METAL IONS, DRUGS AND PESTICIDES USING ORGANIC REAGENTS IN INDUSTRIAL EFFLUENTS.

2. INTRODUCTION

In the past few years, a number of instrumental techniques are developed which are fast, selective and having a high degree of accuracy. A spectrophotometric method of analysis is an excellent tool, which is briefly used for the determination of huge variety of materials. The spectrophotometric technique is the most commonly used method for analysis. Achievement of high accuracy, precision and cost effectiveness is the most important benefit of visual spectrophotometry. Therefore the availability of spectrophotometer made this technique absolute necessary to the modern analytical chemists.

Analytical chemistry plays a very important role in many research areas in chemistry, biochemistry, biology, geology and other sciences and analytical chemist has a very important role in modern society. Thus, most industries do both qualitative and quantitative chemical analysis to find out that the raw materials used meet certain specifications and also to check the quality of product. Analysts have developed large number of instrumental techniques and these techniques are extremely sensitive and can get results rapidly with high accuracy. Some of these methods are inductive coupled-plasma atomic absorption, X-ray fluorescence, HPLC, Voltammeters, UV-VIS spectroscopy etc. These instrumental techniques are essential to the modern analytical chemists. It is most important method for determining metals in alloys, minerals and complexes sensitivity. Spectrophotometry offers the benefits of having calibration graphs that are linear over a wide range. These instruments are with digital readouts or connected to a computer, which provides a high degree of accuracy and an excellent way to determine the metal ion in parts per million levels. The limitation to its use is set by the degree of interference from other metal ion.

In chemistry, spectrophotometry is the quantitative measurement of the reflection or transmission properties of a material as a function of wavelength. The basis of spectrophotometric methods is the simple relationship between the color of a substance and its electronic structure. A molecule or an ion exhibits absorption in the visible or ultra-violet region when the radiation causes an electronic transition in molecules containing one or more chromophoric groups. The color of a molecule may be increase by substituent called auxochromic groups, which displace the

absorption maxima towards longer wavelength (bathochromic shift). The color determining factors in many molecules is by addition of conjugated double bonds.

The importance of the colored solution is based on the fact that the radiation absorbed is characteristic of the material responsible for absorption. Any soluble colored material can be determined quantitatively as well as qualitatively. In addition, a substance that is not colored may often be determined by adding a chromogenic reagent that will convert to an intensively colored species showing strong absorbance in the visible region. This absorbance data can be used for the determination of metal ions and anions in the suitable concentration range in accordance with Beer's law. Proper selectivity can be achieved by controlling the pH, using masking agents etc. It provides an excellent way to determine the metal ions and anions in parts per million.

The quantitative applicability of the absorption method is based on the fact that the number of photons, absorbed is directly proportional to the number or concentration of atoms, ions or molecules. The sequence of events in a spectrophotometer is as follows:

- The light source shines through the sample.
- The sample absorbs light.
- The detector detects how much light the sample has absorbed.
- The detector then converts how much light the sample absorbed into a number.
- The numbers are either plotted straight away

Elements: Metals

Elements present in very small quantity i.e. 10^{-3}-10^{-4} parts by weight in a sample is designated as 'trace elements'. These elements, notwithstanding their low abundance in nature, play a vital role in plant, animal and human nutrition. However they exhibit hazardous effects when their concentration exceeds a certain value [1-2]. Because of their adverse action on immune system and physiology of living beings, some of them are called toxic elements, and these include Pb, Cd, Hg, As, Se, Sb, Cr, etc.[3-4]. Liver, Brain, Lungs, Kidney, Bones and Teeth, RBC & Plasma, Larynx etc. are the target organs in which they are accumulated and affect them. **Hence, the need of a sensitive, selective, simple and reliable method for their determination is clearly recognized.**

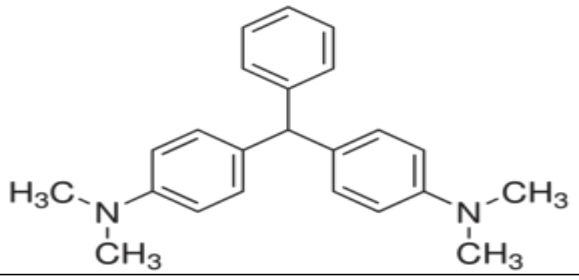
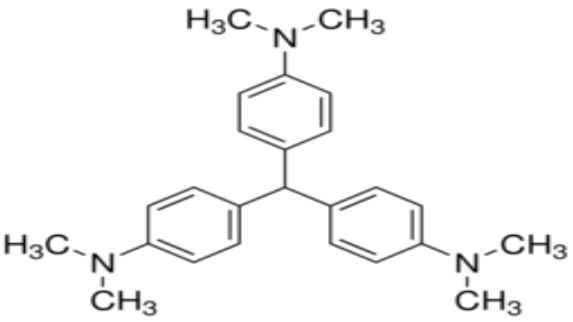
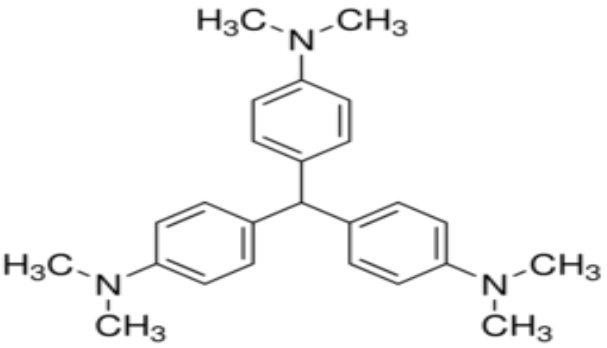
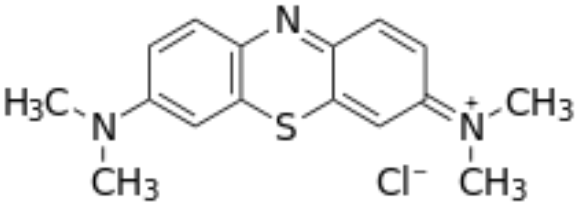
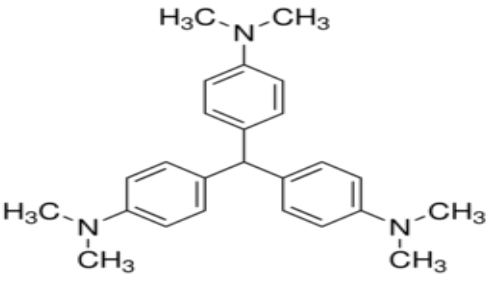
Pesticides

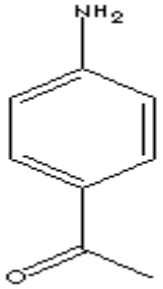
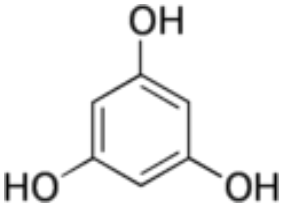
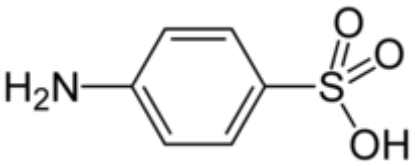
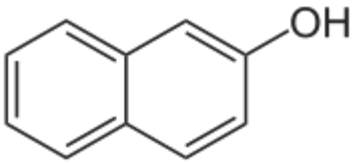
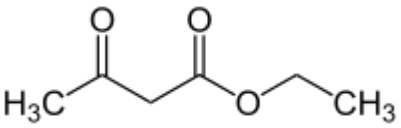
The term pesticide covers a wide range of compounds including insecticides, fungicides, herbicides, rodenticides, molluscicides, nemataticides, plant growth regulators and others [5]. The wide use of agricultural pesticides activates the research towards their environmental effects. They contaminate the environment due to their excess use, solubility in water, volatilization, through water run-off, and chemical degradation the suspended particles of pesticides in air are then removed by rainfall, settling of aerosols, chemical photo-degradation and their diffusion in fog droplets. Their hazardous effects are well known on human beings when exposed over long time. Human beings and other living species ingest the pesticides directly or indirectly from their surroundings i.e. air, water, soil, vegetation, etc. **This indicates the pesticides analysis in various environmental and effluent samples to be an essential tool for the assessment of the contamination level.**

Drugs

A drug is a substance that when put into the body can change the way the body works. In pharmacology, a drug is "a chemical substance used in the treatment, cure, prevention, or diagnosis of disease or used to otherwise enhance physical or mental well-being." A "soft" drug is less addictive and considered less harmful to the body and to society as a whole. A "hard" drug is more addictive and considered much more harmful to the body and society in general. Psychoactive drugs are drugs that change our feelings, our perceptions and even behavior. Psychoactive drugs bring a chemical reaction in the brain causing feelings, thoughts and behavior to be affected. A legal drug is a drug that can be obtained either by prescription or over the counter and used in the prescribed and appropriate. An illegal drug is a drug that is not approved by law for use in this country. It is well known that the quantity of any drug should essential to overcome any disease. **So quantitative analysis of drugs is essential to find out its effect on any disease or human body.**

In this proposed plan of research study we will develop new, sensitive and selective spectrophotometric methods for some of species belongs to the above described heading i.e. Cr, Te, Sb, Organophosphate, Paracetamol, Aspirin etc using new chromogenic and coupling agents. The validity of developed method will be checked by applying these methods in detection and determination of analyte in samples of different origin. The following reagents will be used in the determination of above species-

S.NO.	REAGENTS	STRUCTURE
1.	Leuco Malachite Green	
2.	Leuco Crystal Violet	
3.	Rhodamine B	
4.	Methylene blue	
5.	Thionine	

6.	P-aminoacetophenone	
7.	Phloroglucinol	
8.	Sulphanillic acid	
9.	B-napthol	
10	Ethyl acetoacetate	

3. A BRIEF REVIEW OF THE WORK ALREADY DONE IN THE FIELD-

Many work done in the field of spectrophotometric determination, some are based on metals some are pesticides, some are ions. Acerda, M.T.Oms (1998) has given a sequential injection sandwich technique for the detection of nitrate and nitrite [6]. Revansidappa and T.N.Kiran kumar (2001) determine trace amounts of chromium with citrazinic acid [7]. A. Asthana *et al* (2002) describe a thin layer chromatographic separation method for herbicides and related compound vie hydrolysis and oxidative coupling [8]. T.N.Kiran Kumar *et al* (2005) develop determination of vanadium using variamine blue [9]. K.K.Tiwari *et al* (2005) describe new method for chromium determination in biological sample with lecocrystal violet [10]. Chand Pasha and Badiaka Narayana (2006) gave a highly sensitive spectrophotometric method for the determination of iodate by using leuco xyelene cyanol FF [11]. Sunita b.Methew *et al (*2006) describes spectrophotometric method for organophosphorus and insecticides like malathion, dimethodate and phorate [12]. Paramane S, Kothapalli L. *et al* (2006) gave a simultaneous spectrophotometric estimation of gatifloxacin and ornidazole in tablet dosage form [13]. P. Reddy Prasad *et al* (2007) has done their spectrophotometric work on tellurium which reacts with leuco malachite green. [14] A.G.Murugeson *et al* (2009) describes isolation and characterization of cypermethrin utilizing bacteria from brinjal cultivated soil [15]. Doppenschmitt S.A. (2010) studied the simultaneous determination of chloromophenol and prednisolone acetate [16].

4. OBJECTIVES OF THE PROPOSED WORK-

- Development of new, cost effective, sensitive and selective spectrophotometric method for the determination of metals ions, drugs and pesticides in samples of different industrial effluents.
- Optimization of analytical parameter like pH, reagent concentration range, temperature and electrolyte effect, diverse ions effects etc.
- Study of stastical parameter, standard deviation, relative standard deviation, coefficient of variance, slope and intercept, absolute and relative error, F & T test, confidence level to check the reliability, reproducibility of developed method.

- The validity of the developed method will be checked by applying the method in determination of analyte in industrial and pharmaceutical effluents from different locations.

5. NOTEWORTY CONTRIBUTION IN THE FIELD OF PROPOSED WORK

Limited work in the field of spectrophotometric determinations reported, Prakash R. *etal* (1991) use malachite green as reagent for determination of chromium [17]. Joyce Vanisha Das and V.K. Gupta (1997) gave an extractive spectrophotometric method using crystal violet for the determination of methoxyethylmercury chloride (fungicide) in environmental and biological samples [18]. Amin A.S. and Raqudp G.H.(2004) describe determination of cephalosporin's in pure form and pharmaceutical formulations [19]. K.K.Tiwari *et al* (2005) gave a new spectrophotometric method for the determination of chromium in environmental and biological samples [20]. Ashok Kumar (2008) gave a synergistic extraction and spectrophotometric determination of palladium (II), Iron (III) and tellurium (V) [21]. Kamlesh Shrivas *et al.* (2008) gave on-site spectrophotometric determination of antimony in water, soil and dust samples [22]. Mohmoud A Omur *et al.* (2009) describe kinetic spectrophotometric determination of certain cephalosporin [23]. Alkhani *et al* (2010) use low conc. of malachite green by high performance phase for chromium determination [24]. Hossein Tavallali *et al* (2011) gives spectrofluorometric determination of paracetamol in pharmaceutical formulation [25]. R.S.Dhundhel and M.K.Rai (2011) developed a new method for the determination of cypermethrin by using p-aminoacetophenone[28]. Ramesh L. Sawant *et al* (2012) gave spectrophotometric estimation of paracetomol and promethazine in tablet dosage forms [26]. Riyad Ahmed Al-Okab *et al* (2012) describe highly sensitive method for determination of paracetamol with iron (III) [27].

6. PROPOSED METHODOLIOGY

1. Literature survey will be performed to identifying which method is most suitable for which metal ion, drug and pesticides and its demerits which should overcome to increase sensitivity of the method.
2. Development of new simple and sensitive spectrophotometric method using organic reagents like leuco crystal violet, leuco malachite green, methelyene blue, Rhodamine B and new coupling agents like p-aminoacetophenone etc. for the detection and determination of Cr, Te, Sb, paracetamol, organophosphosphate and Cypermethrin.

3. Proposed method for detection of Cr is based on the reaction of chromium (III/VI) with acidified potassium iodide to liberate iodine. The liberated iodine selectively oxidizes leuco malachite green in the presence of acidic buffer.
4. Detection of Tellurium (II/IV) using leuco crystal violet.
5. Determination of Antimony (III/V) using thionine.
6. Detection of paracetamol is based on the hydrolysis of paracetamol in acidic or alkaline medium to produce p-aminophenol which is diazotized. The diazotized p-aminophenol undergoes coupling reaction with new coupling agents.
7. Determination of organophosphorus pesticides (Malathion, dimethoate, and phorate) will be based upon oxidation of leuco malachite green by KIO_3 in hydrochloric acid medium to give malachite green dye or by addition of Ce (IV) in sulphuric acid media, and unreacted oxidant is determined by decreasing the violet colour of crystal violet.
8. Determination of cypermethrin by alkaline hydrolysis of cypermethrin, release cyanide. The cyanide will be treated with bromine and pyridine to form glutaonic aldehyde which will be coupled with new coupling agent to give azo dye.
9. Optimization of analytical parameters like pH, reagent concentration, temperature and diverse ion effects etc.
10. Study of statistical parameters viz. standard deviation, relative standard deviation, correlation coefficient, molar absorptivity, sandell's sensitivity etc.
11. Proposed method should apply in different industrial effluent samples by recovery test to check their selectivity and sensitivity.

7. EXPECTED OUTCOMES OF THE PROPOSED WORK

- The proposed work spectrophotometric determination of metal ions, drugs & pesticides using organic reagents will be low cost might be preferred in small laboratory is good alternative of other costly instrumental methods like atomic absorption, flurometry, gas chromatography etc.
- It also overcomes many shortcomings of other spectrophotometric methods reported by different researcher's viz.sensitivity, selectivity, interference of ions and their wide applicability.
- It will applicable to analyze, detection & determination of large variety of samples from different origins.

- This will help for quick and timely assessment of the concentration level in the environment contaminated with these species.

- It will introduce awareness to the common people to understand health effect of various contaminations.

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9. LIST OF PUBLISHED PAPERS-

1.Paper presented in National Conference

Paper entitled "A Facile Spectrophotometric Method for the Determination of Hydrazine with Methyl Orange" presented in 31st conference of Indian council of chemists at department of chemistry Saurashtra University Rajkot on 26th-28th December 2012.

2. Seminar

National seminar "Changing environment and its impact on biodiversity" 11-12 October, 2012, organized by department of botany Govt. D. B. Girls P. G. Autonomous College Raipur (C.G.).

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